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Rigorous theoretical investigation of the ground state of H_2

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A variety of results are reported for the ground state ($X\,^1\Sigma_g^+$) of the hydrogen molecule. They include improved Born-Oppenheimer calculations, a study of the convergence of energies with basis-set size, adiabatic calculations, and the first successful *ab initio* nonadiabatic calculation. The latter, which treats H_2 as a four-body problem, leads us to predict that the dissociation energy of H_2 is 36117.92 cm^{-1}. This value may be compared with 36 117.8 ± 0.4 cm^{-1} (the value derived from the experimental ionization potential), with 36118.6 ± 0.5 cm^{-1} (the value derived from the experimental vibrational levels of the $B\,^1\Sigma_u^+$ state), or with 36118.3 cm^{-1} (the upper-bound value derived from the experimental absorption limit).

I. INTRODUCTION

This paper is concerned with highly accurate solutions of the Schrödinger equation for the hydrogen molecule in its lowest electronic state ($X\,^1\Sigma_g^+$). The reasons for undertaking the calculations reported here were (i) to obtain an independent verification of the pioneering Born-Oppenheimer and adiabatic calculations of Kołos and Wolniewicz, (ii) to explore the convergence properties of the basis sets used and to find a logical way of choosing basis functions, (iii) to carry out a full nonadiabatic calculation (i.e. treating H_2 as a four-body problem) of the lowest nonrotational energy level, and (iv) to determine as accurately as possible the dissociation energy of H_2.

The rationale behind the first two reasons is self-evident, the third reason is founded on the fact that the only previous nonadiabatic calculation[1] for H_2 was unsuccessful insofar as it gave a ground-state energy higher than the adiabatic value.[2] This was due to the use of too small a basis set. The fourth reason is related to the known discrepancy between the theoretical and experimental dissociation energy of H_2.[3,4] In essence, the work is a logical extension of our recently published H_2^+ calculations[5-7]: the techniques which we found successful for H_2^+ are now applied to H_2.

The paper conveniently falls into three parts which reflect the three levels at which the Schrödinger equation can be solved: Born-Oppenheimer (BO), adiabatic, and nonadiabatic. Excluding radiative effects, the complete nonrelativistic Hamiltonian in the center-of-mass system for H_2 may be written as

$$H = H^0 + H' , \tag{1}$$

$$H' = H_1' + H_2' , \tag{2}$$

where, using atomic units (1 hartree = 2 R_∞ ≃ 219 474.64 cm^{-1} and 1 bohr = a_0 ≃ 0.529 177 06 Å),

$$H^0 = \tfrac{1}{2}(\nabla_1^2 + \nabla_2^2) - r_{1a}^{-1} - r_{1b}^{-1} - r_{2a}^{-1} - r_{2b}^{-1} + r_{12}^{-1} + R^{-1} , \tag{3}$$

$$H_1' = -(8\mu)^{-1}(\nabla_1^2 + \nabla_2^2 + 2\nabla_1 \cdot \nabla_2) , \tag{4}$$

$$H_2' = -(2\mu)^{-1}\nabla_R^2 . \tag{5}$$

In these equations ∇_i^2 is the Laplacian operator for electron i relative to the *geometric* center of the nuclei; ∇_R^2 is the Laplacian operator for one nucleus (a) relative to the other (b); r_{ia}, r_{12}, and R are the distance of electron i from nucleus a, the interelectronic distance and the internuclear distance, respectively; μ is the reduced nuclear mass and equals $m_p/2m_e$ where the electron-proton mass ratio (m_e/m_p) is 0.000 544 617.[8] If ξ_i, η_i, ϕ_i are the usual elliptical coordinates of the ith electron, then for nonrotational states[9]

$$\nabla_i^2 = (4/R^2)X_i ,$$

$$r_{ia}^{-1} + r_{ib}^{-1} = (4/R)\xi_i(\xi_i^2 - \eta_i^2)^{-1} ,$$

$$\nabla_1 \cdot \nabla_2 = (4/R^2)(\xi_1\eta_1\xi_2\eta_2A_1A_2 + B_1B_2 - \xi_1\eta_1A_1B_2 - \xi_2\eta_2B_1A_2 + M\cos\phi A_1A_2) ,$$

$$\nabla_R^2 = \frac{\partial^2}{\partial R^2} + \left(\frac{2}{R}\right)\frac{\partial}{\partial R} + \left(\frac{2}{R^2}\right)Y_1Y_2 - \left(\frac{2}{R^2}\right)(Y_1 + Y_2)\left(1 + R\frac{\partial}{\partial R}\right) + \left(\frac{1}{R^2}\right)[(\xi_1^2 + \eta_1^2 - 1)X_1 + (\xi_2^2 + \eta_2^2 - 1)X_2] + \left(\frac{2}{R^2}\right)M\cos\phi B_1B_2 ,$$

$$X_i = (\xi_i^2 - \eta_i^2)^{-1}\left(\frac{\partial[(\xi_i^2 - 1)\partial/\partial\xi_i]}{\partial\xi_i} + \frac{\partial[(1 - \eta_i^2)\partial/\partial\eta_i]}{\partial\eta_i}\right) ,$$

$$Y_i = (\xi_i^2 - \eta_i^2)^{-1}\left(\xi_i(\xi_i^2 - 1)\frac{\partial}{\partial\xi_i} + \eta_i(1 - \eta_i^2)\frac{\partial}{\partial\eta_i}\right) ,$$

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$$A_i = (\xi_i^2 - \eta_i^2)^{-1}\left(\xi_i \frac{\partial}{\partial \xi_i} - \eta_i \frac{\partial}{\partial \eta_i}\right),$$

$$B_i = (\xi_i^2 - \eta_i^2)^{-1}\left(\eta_i \frac{\partial}{\partial \xi_i} - \xi_i \frac{\partial}{\partial \eta_i}\right),$$

$$M = [(\xi_1^2 - 1)(\xi_2^2 - 1)(1 - \eta_1^2)(1 - \eta_2^2)]^{1/2},$$

$$\phi = \phi_1 - \phi_2 .$$

In the BO approximation the calculation of the rovibronic energies proceeds in two parts: first the calculation of the potential-energy curve $E^0(R)$ from

$$H^0\Psi_B = E^0(R)\Psi_B \qquad (6)$$

(Ψ_B are the BO electronic wave functions) and then, using this curve, the solution of the vibrational-rotational Schrödinger equation to obtain the final rovibronic energies. The adiabatic approximation in its *usual* form (a variation of the method is also considered in Sec. III) differs from the BO method by using $U(R)$ in place of $E^0(R)$, where

$$U(R) = \langle \Psi_B | H^0 + H' | \Psi_B \rangle$$
$$= E^0(R) + \Delta E'(R) . \qquad (7)$$

The nonadiabatic calculation requires the solution of the exact complete nonrelativistic nonradiative Schrödinger equation:

$$H\Psi = E\Psi , \qquad (8)$$

where Ψ are wave functions involving explicitly both nuclear and electronic coordinates and the eigenvalues E are the rovibronic energy levels.

All the calculations were performed on an IBM 360/65 computer in double precision and, unless stated otherwise, the integrals were evaluated by the methods in Refs. 10 and 11 except that Gauss-Legendre quadrature was used in place of Simpson's rule. All integrals are accurate to at least nine significant figures.

II. BORN-OPPENHEIMER CALCULATIONS

Equation (6) was solved by using the variational wave function:

$$\Psi_B = \sum_{i=1}^{N} c_i [\Phi_i(1,2) + \Phi_i(2,1)] , \qquad (9)$$

where

$$\Phi_i(1,2) = e^{-\alpha_1\xi_1} e^{-\alpha_2\xi_2} \xi_1^{m_i} \xi_2^{n_i} \eta_1^{k_i} \eta_2^{l_i} \rho^{q_i}$$
$$\times [e^{\beta_1\eta_1 + \beta_2\eta_2} + (-1)^{k_i + l_i} e^{-\beta_1\eta_1 - \beta_2\eta_2}] \qquad (10)$$

and

$$\rho = 2r_{12}/R .$$

TABLE I. Convergence of $E^0(R)$ with basis-set size at $R = 1.4$ bohrs.

Basis set	N[a]	$E^0(R)$ (hartrees)
(6453/5)	130	−1.174 475 36
(6453/6)	194	−1.174 475 62
(6453/7)	249	−1.174 475 65
(5342/7)	176	−1.174 475 55
(6453/7)	249	−1.174 475 65

[a] Total number of basis functions.

It should be noted that the powers m_i, n_i, etc., are integers ≥ 0 and that there are four nonlinear parameters (α_1, α_2, β_1, β_2) which may be optimized with some difficulty, and N linear parameters c_i which may readily be found by solving the usual secular equation.

The key to the solution of Eq. (6) lies in finding an efficient and logical way for selection of the basis functions Φ_i. We have found that it is not satisfactory to simply add basis functions one at a time and to retain or exclude a function on the grounds of the energy drop. Quite often a function which at first sight gives little improvement to the energy *will* do so when further terms are added. After much trial and error we have concluded that if we denote the wave function Ψ_B as $(a_0a_1a_2\cdots/b)$, where $a_p = \max(m_i + k_i) = \max(n_i + l_i)$ for $q_i = p$ and $b = \max(m_i + n_i + k_i + l_i)$ for any value of q_i (the power of ρ), and include all basis functions within these constraints, then raising $a_0, a_1\cdots$ in concert and separately raising the value of b is an efficient test of convergence.

In Table I we present results for $R = 1.4$ bohrs and with $\alpha_1 = \alpha_2 = 1.117$ and $\beta_1 = \beta_2 = 0$. For this situation symmetry requires that $k_i + l_i$ be even. The value of $\alpha_1 (= \alpha_2)$ was determined by minimizing $E_0(1.4)$ for the wave function (5342/5) which contains 107 terms. We checked our programming by reproducing the energy that Kołos and Rychlewski (KR) obtained for the 80-term (b) wave function listed in Table I of Ref. 12. We also tested the effect of adding basis functions containing powers of ρ higher than 3 [i.e., $\Psi_B = (a_0a_1a_2a_3a_4/b)$] but found that the energy lowering was less than 10^{-8} hartrees. Consequently, we restricted ourselves to wave functions of the form $(a_0a_1a_2a_3/b)$. The first three rows in Table I show that our basis set (6453/7) has converged to within 0.01 cm^{-1} with respect to changes in b, and the last two rows show that it has converged to within 0.02 cm^{-1} with respect to raising a_0, a_1, a_2, a_3 together.

Kołos and Rychlewski[12] have used the same type of wave function as Eq. (10) but they optimized

TABLE II. Comparison of $E^0(R)$ values (hartrees).

R (bohrs)	$E^0(R)$, Ref. 2 [a]	$E^0(R)$, this work [b]	Difference (cm^{-1})
1.3	−1.172 346 23	−1.172 347 08	0.19
1.4	−1.174 474 77	−1.174 475 65	0.19
1.5	−1.172 854 08	−1.172 855 00	0.20

[a] 100-term wave function.

[b] Basis set (6453/7).

all four nonlinear parameters α_1, α_2, β_1, and β_2 for a 40-term expansion. They then used these parameter values in a 130-term expansion for $R = 1.4$ bohrs and found $E^0 = -1.174\,475\,40$ hartrees, only 4×10^{-8} hartrees lower than the value for our 130-term function. The latter, it should be noted, contains only *one* nonlinear parameter ($\alpha_1 = \alpha_2$). Table I shows that with a few more terms we can obtain lower energies than KR even though we keep $\alpha_1 = \alpha_2$ and $\beta_1 = \beta_2 = 0$. This is an important point since not only are linear parameters easier to optimize than nonlinear ones but the basic integrals are easier to evaluate when $\beta_1 = \beta_2 = 0$; there will also be fewer integrals.

Previously the best determination of $E^0(R)$ near the equilibrium internuclear distance ($R = 1.4$ bohrs) has been that given by Kołos and Wolniewicz[2] for a 100-term expansion of the same form as used here; in Table II we compare those results with our (6453/7) wave function at $R = 1.3$, 1.4, and 1.5 bohrs with $\alpha_1 = \alpha_2 = 1.117$ and $\beta_1 = \beta_2 = 0$. There is a significant and almost constant improvement of 0.19 cm^{-1}. We therefore conclude that all potential curves based on the results of Ref. 2 should be lowered by 0.19 cm^{-1} in the region 1.3–1.5 bohrs. We should emphasize that this drop is only partly a result of having a larger basis set since even the wave function (5342/5), with only 107 terms, gives an energy (−1.174 475 28 hartrees) which is 0.11 cm^{-1} lower than the 100-term function of Ref. 2 at $R = 1.4$ bohrs. Once again, *choice* of basis functions is as important as the number of basis functions.

III. ADIABATIC CALCULATIONS

We have calculated the adiabatic energy $U(R)$, see Eq. (7), near $R = 1.4$ bohrs using the wave function (5342/5) with $\alpha_1 = \alpha_2 = 1.117$, $\beta_1 = \beta_2 = 0$. We have assumed that $d\alpha/dR$ is zero since Pritchard and Wolniewicz[13] estimate that the error in doing so will only amount to a few hundredths of a cm^{-1}. This error will decrease with an increase in the number of linear parameters (c_i) and so should be less for our wave function than for the one used in Ref. 13. We have used a numerical method to find the derivatives dc_i/dR, i.e.,

$$\frac{dc_i(R)}{dR} = \frac{c_i(R+\Delta R) - c_i(R-\Delta R)}{2\Delta R}$$

with $\Delta R = 5\times10^{-5}$ bohrs. This approximation appears valid since the results obtained using it agree with those of Kołos and Wolniewicz[11] who used an analytical method for finding dc_i/dR.

The adiabatic correction $\Delta E'(R)$ may be split into two parts

$$\Delta E'(R) = \Delta E_1' + \Delta E_2' , \tag{11}$$

where

$$\Delta E_1' = \langle \Psi_B | H_1' | \Psi_B \rangle , \tag{12}$$

$$\Delta E_2' = \langle \Psi_B | H_2' | \Psi_B \rangle , \tag{13}$$

and H_1' and H_2' are defined by Eqs. (4) and (5), respectively. The results are given in Table III under the heading method I, and the total corrections differ from those of Ref. 11 by about 0.02 cm^{-1}; the major part of this discrepancy is in the $\Delta E_2'$ component. A correction has been made to the values in Ref. 11 for a change in the proton-electron mass ratio. The differences are given in the column headed Δ_1. Since only a 54-term wave function was used in Ref. 11, it is clear that $\Delta E'$ is not very sensitive to the quality of Ψ_B. We may note for the sake of comparison that the change in $E^0(1.4)$, the BO energy, in going from the 54-term wave function[11] to the (5342/5) wave function is about 1.0 cm^{-1}.

An alternative approach to calculating adiabatic corrections has been given by Pritchard and Wolniewicz[13]; we will call this method II. They propose calculating the BO energy with the operator $H^0 + H_1'$. $\Delta E_1'$ could then be defined by

$$\Delta E_1' = \langle \Psi_B^\dagger \,|\, H^0 + H_1' \,|\, \Psi_B^\dagger \rangle - \langle \Psi_B \,|\, H^0 \,|\, \Psi_B \rangle \tag{14}$$

and $\Delta E_2'$ by

$$\Delta E_2' = \langle \Psi_B^\dagger \,|\, H_2' \,|\, \Psi_B^\dagger \rangle . \tag{15}$$

The BO wave function in this treatment, $\Psi_B^\dagger$, differs very slightly from Ψ_B by virtue of small changes in the linear parameters (c_i) caused by adding H_1' to H_0. We have verified the results of Ref. 13 and find that there is little difference between using the 54-term wave function of that

TABLE III. Adiabatic corrections (cm^{-1}).[a]

R (bohr)	Method I		Method II				
	$\Delta E_1'$	$\Delta E_2'$	$\Delta E_1'$	$\Delta E_2'$	$\Delta E'$ [b]	Δ_1 [c]	Δ_2 [d]
1.30	79.780	38.203	79.760	38.183	118.005	0.023	0.062
1.35	77.962	38.264	77.942	38.244	116.250	0.024	0.064
1.40	76.253	38.341	76.234	38.321	114.618	0.024	0.063
1.45	74.646	38.434	74.627	38.415	113.103	0.022	0.061
1.50	73.135	38.546	73.117	38.526	111.702	0.021	0.059

[a] Except for the sixth column the basis set is (5342/5).

[b] The total adiabatic correction from Ref. 11, using a 54-term wave function, but corrected to account for more recent mass values.

[c] Column 6 less the sum of columns 2 and 3.

[d] Column 6 less the sum of columns 4 and 5.

reference or our (5342/5) wave function. The adiabatic correction differs by about 0.06 cm^{-1} (see the column headed Δ_2 in Table III) from the results given in Ref. 11. The implication is therefore that method II decreases the adiabatic correction by about 0.04 cm^{-1} in comparison with method I. This is the same conclusion as the one reached by Pritchard and Wolniewicz.[13]

IV. NONADIABATIC CALCULATIONS

For the nonadiabatic calculations we solved the complete nonrotational Schrödinger equation

$$H\Psi = E\Psi\,, \tag{16}$$

where H is defined by Eq. (1) and Ψ is expanded as

$$\Psi = \sum_{i=1}^{N} \sum_{j=0}^{M} c_{ij}[\Phi_i(1,2) + \Phi_i(2,1)]\chi_j\,. \tag{17}$$

The radial functions are defined by

$$\chi_j = R^{-3} e^{-x^2/2} H_j(x)\,, \tag{18}$$

where $x = \gamma(R-\delta)$ and $H_j(x)$ are the usual Hermite polynomials. Since we are only considering nonrotational energies, the nuclear-angular coordinates do not appear in Eq. (17). For the electronic functions in Eq. (17) we use those defined by Eq. (10) and the basis set (5342/5), 107 terms, with $\alpha_1 = \alpha_2 = 1.117$ and $\beta_1 = \beta_2 = 0$. The other nonlinear parameters γ and δ are fixed at 4.3 and 1.4, respectively, the former number being estimated from the harmonic force constant for H_2, and the latter being the equilibrium internuclear distance. The wave function Ψ is a natural extension of the type of nonadiabatic wave function we used successfully for H_2^+,[7] and in that work we found that with a large basis set the results were not sensitive to the choice of γ and δ.

It should be mentioned that the usual techniques for solving secular equations do not work here, where we have very large nonsparse matrices, and consequently we have developed a new method which is described elsewhere[14].

We have tested the convergence of Ψ with respect to the number of radial functions χ_j, by finding the lowest-energy level when $0 \leq j \leq 8$ (nine radial functions) and when $0 \leq j \leq 9$ (ten radial functions) giving a 963- and 1070-term wave function, respectively. For the 963-term wave function the lowest energy is −1.164 024 11 hartrees and for the 1070-term wave function it is −1.164 024 13 hartrees, suggesting that the energy has converged, in terms of radial basis functions, to within 0.01 cm^{-1}. For overall convergence, a crude comparison with the convergence of the H_2^+ results in Ref. 5 suggests that the energy −1.164 024 13 hartrees is within 0.2 cm^{-1} of the true nonadiabatic lowest energy of H_2. This result is the first successful non-approximate nonadiabatic calculation of the lowest-energy level of H_2. Previously Kołos and Wolniewicz[1] used a 147-term wave function but it was so inadequate that their energy was *above* the best adiabatic value available at that time. We have confirmed our nonadiabatic calculations by reproducing their 54-term result. This shows that their calculation is error free and we can therefore say that the inadequacy of their 147-term wave function lies in having an insufficient number of electronic and radial functions.

The lowest-energy level may be used to determine the dissociation energy of H_2. However, before comparison with experiment can be made, two corrections (relativistic and radiative) must be considered. Using the data in Ref. 15 the vibrational-rotational Schrödinger equation can be solved with and without the relativistic energy added to $U(R)$ and this leads to a correction to the dissociation energy of −0.54 cm^{-1}. The radiative correction has been calculated by Garcia[16] to be -0.22 ± 0.03 cm^{-1}. Furthermore, our BO calculations show that changing from a (5342/5) to a

TABLE IV. Dissociation energy D_0 of the hydrogen molecule (cm^{-1}).

Nonadiabatic	36 118.60
Basis-set correction	0.08
Relativistic correction	−0.54
Radiative correction	−0.22
Total theoretical energy	36 117.92
Semiempirical [a]	36 117.8 ± 0.4
Experimental [b]	36 118.6 ± 0.5

[a] From the theoretical dissociation energy of H_2^+ and the experimental ionization potential of H_2.

[b] From Ref. 4.

(6453/7) basis set lowers $E^0(1.4)$ by 0.08 cm^{-1}, therefore it would not be unreasonable to expect the same decrease in the nonadiabatic energy if the larger basis set had been used to put Ψ together. In Table IV we combine these results and show that the dissociation energy is 36 117.92 cm^{-1}. This is a lower limit but we believe it to be within about 0.1 cm^{-1} of the true value. Stwalley[4] has analyzed the experimental vibrational levels of the $B\,^1\Sigma_u^+$ state and concludes that the experimental ground-state dissociation energy is 36 118.6 ± 0.5 cm^{-1}, so that even if one takes the maximum experimental error bound there is still a difference of 0.2 cm^{-1} between theory and experiment, of which only 0.1 cm^{-1} could be picked up by further improvement in the nonadiabatic calculation.

One may obtain a semiempirical value for the dissociation energy by combining the theoretical dissociation energy of H_2^+ (Ref. 17) $[D_0(H_2^+)]$ with the experimental ionization potential (P_I) of H_2 (Ref. 18) and the energy of the hydrogen atom (corrected for radiative and relativistic effects) $[E(H)]$:

$$\begin{aligned} D_0(H_2) &= D_0(H_2^+) + P_I(H_2) + E(H) \\ &= 21\,379.4 + 124\,417.2\ (\pm 0.4) - 109\,678.8 \\ &= 36\,117.8 \pm 0.4\ \mathrm{cm}^{-1}. \end{aligned}$$

This value is in good agreement with our theoretical value but one notes that only at the limit of the error bar does it come within the region of the previous "experimental" value.

Herzberg[19] from ultraviolet absorption studies of H_2 has determined that the dissociation energy lies between 36 118.3 and 36 116.3 cm^{-1} but favors the upper limit. Our value falls within his range and *is* closer to the upper value.

Since there have until now been no acceptable nonadiabatic calculations for H_2, many theoreticians have made approximate estimates of the nonadiabatic correction, i.e. the difference between the adiabatic and nonadiabatic dissociation energy, and it is of interest to compare these estimates with the results in this paper. We have calculated the lowest adiabatic energy from the data in Ref. 15 and corrected the result in two ways: (a) a correction of 0.11 cm^{-1} for using our 107-term BO wave function (which is more appropriate in view of the basis functions used in the nonadiabatic wave function) in place of the Kołos and Wolniewicz[2] 100-term wave function for calculating $E^0(R)$, see Sec. II; and (b) a correction of 0.02 cm^{-1} to the adiabatic correction for using the 107-term wave function in place of the Kołos and Wolniewicz[11] 54-term wave function in calculating $\Delta E'(R)$, see Sec. III. We then find the adiabatic energy (method I) of the lowest level to be −1.164 022 20 hartrees and, if we compare this value directly with the 1070-term nonadiabatic energy of −1.164 024 13 hartrees, we have a nonadiabatic correction of 0.42 cm^{-1}. If method II is used to find the adiabatic energy then the correction will be 0.04 cm^{-1} smaller (see Sec. III), i.e. 0.38 cm^{-1}. It is clear that either of these values can be considered to be the nonadiabatic correction since the adiabatic energy can be defined in more than one way.

Bunker[20] has compared the vibrational spacings obtained from adiabatic calculations (method I) with the experimental spacings. By a fit of these differences (attributed to nonadiabatic effects[21]) to a polynomial in the vibrational quantum number he deduced the nonadiabatic change to the individual levels and concluded that the correction to the dissociation energy is 0.43 cm^{-1}. This result is in excellent agreement with our value.

LeRoy and Bernstein[22] have used the treatment developed by Van Vleck[23] which in turn was based on second-order perturbation theory. Unfortunately it makes use of the Unsöld approximation which requires knowledge of the mean excitation energy ΔE_{av}, a quantity which is notoriously difficult to estimate. The value LeRoy and Bernstein took was 1.35×10^5 cm^{-1} and this is probably too low if the H_2^+ value is any guide[5]. They then found the nonadiabatic correction to be 0.65 cm^{-1}. A larger value of ΔE_{av} would reduce this number. Kołos and Rychlewski[12] have used this value of 0.65 cm^{-1} to estimate the dissociation energy of H_2 and consequently they obtain a larger energy than we have reported here. We might also note that the adiabatic-relativistic-radiative dissociation energy they quote (36 117.33 cm^{-1}) is 0.04 cm^{-1} larger than our value. This is because the value quoted is based on $m_p/m_e = 1836.12$ rather than on the more recent mass ratio given in Ref. 8; this point has been discussed before.[15]

Bishop and Shih[15] have used an effective Schrödinger equation involving a single variable parameter to determine the nonadiabatic energy levels of H_2 and D_2. The parameter is chosen so that there is the best possible fit to the experimental energy spacings. This method predicts a nonadiabatic correction to the dissociation energy of H_2 of 0.49 cm^{-1}.

Approximately, the ratio of the nonadiabatic correction for the lowest level for H_2 to that for D_2 is $(\mu_{D_2}/\mu_{H_2})^{3/2} \simeq 2.8$, see Eq. (31) of Ref. 5. So that we estimate the nonadiabatic correction to the dissociation energy of D_2 to be 0.42/2.8 = 0.15 cm^{-1}. We have calculated the adiabatic-relativistic-radiative dissociation energy from the data of Table III of Ref. 15 to be 36 747.93 cm^{-1}. If we correct this value by 0.19 cm^{-1} for improvement in the BO energy curve (see Sec. II) and add the nonadiabatic correction, we find the approximate theoretical dissociation energy of D_2 to be 36 748.27 cm^{-1}. This may be compared with the experimental values of 36 748.88 (±0.3) (Ref. 3) and 36 748.9 (±0.4) cm^{-1} (Ref. 19).

It is tempting to use the wave function in Eq. (17) to calculate the higher nonrotational nonadiabatic energy levels but extreme caution must be applied since (a) more radial basis functions (χ_j) will be needed and (b) the form of the electronic part of the wave function is not as appropriate when, on average, the internuclear distance is different from 1.4 bohrs (as it will be for the excited states). With 13 radial basis functions and 107 electronic basis functions (giving a nonadiabatic wave function with 1391 terms) the second root of the secular equation is −1.145 063 41 hartrees while the lowest root is −1.164 024 15 hartrees (only 2×10^{-8} hartrees lower than the value given by the previous 1070-term wave function). These values lead to a transition frequency, corrected by 0.024 cm^{-1} for relativistic effects, of 4161.425 cm^{-1} for the transition between the two lowest nonrotational states of H_2. This value may be compared to the experimental one[24] of 4161.178 cm^{-1}. The discrepancy is undoubtedly due to our not having enough electronic basis functions for calculating the excited state. We do believe, however, that we have sufficient *radial* basis functions since with one fewer the excited energy level changes by less than 0.02 cm^{-1}. The adiabatic-relativistic transition frequency between the two lowest nonrotational states of H_2 is 4162.046 cm^{-1} (Ref. 15).

It should be mentioned that Atabek and coworkers[25] have applied multichannel quantum-defect theory to the molecular Rydberg states of H_2 and D_2. This theory includes both adiabatic and nonadiabatic effects. They have obtained rovibronic levels for the *B* and *C* states and the agreement with the experimental levels is to within a few cm^{-1}.

V. CONCLUSIONS

Our essential results are as follows. For BO calculations near $R = 1.4$ bohrs the wave function in Eq. (9) can be simplified without loss of accuracy by letting $\alpha_1 = \alpha_2$ and $\beta_1 = \beta_2 = 0$ as was done originally by Kołos and Wolniewicz.[2] To achieve accurate results it is necessary to increase the basis-set size in an orderly manner. By doing this we have obtained BO energies which have converged to within 10^{-7} hartrees and are approximately 0.2 cm^{-1} lower than those of Ref. 2 which have been the standard values for the past decade.

Our adiabatic calculations confirm the results of Pritchard and Wolniewicz[13], i.e. a relatively small basis set is sufficient for calculating the adiabatic correction and a different formulation of the adiabatic problem (method II) lowers the adiabatic correction by about 0.04 cm^{-1}.

From our nonadiabatic calculations we conclude that the dissociation energy of H_2 is 36 117.92 cm^{-1} which compares favorably with the value deduced from the experimental ionization potential but is just outside the limits of the "experimental" value given by Stwalley (36 118.6 ± 0.5 cm^{-1}). It is within the limits given by Herzberg[19], however these limits are quite wide.

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